

UNIVERSITY OF PENNSYLVANIA

THE BEHAVIOR OF GERMANIUM
TETRACHLORIDE AND RELATED
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OUS CHLORIDE, WITH CONCEN-
TRATED HYDROCHLORIC ACID

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A THESIS

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

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THE BEHAVIOR OF GERMANIUM TETRACHLORIDE AND RELATED CHLORIDES, ESPECIALLY ARSENIOS CHLORIDE, WITH CONCENTRATED HYDROCHLORIC ACID

BY ELTON R. ALLISON

Procedures for the separation of germanium from arsenic have followed two general methods: the distillation of germanium tetrachloride from a hydrochloric acid solution of germanium dioxide under conditions which keep arsenic in the pentavalent state of oxidation, and the precipitation of arsenic as sulfide under conditions which prevent the precipitation of germanium sulfide. The method proposed by Dennis and Johnson,¹ using a current of chlorine and a special still head, is the most efficient distillation process. Abrahams and Müller² have recently described a method for the sulfide separation which is particularly valuable for analytical purposes.

The purpose of this investigation was to study an extraction method for the removal of arsenious chloride from germanic chloride. Friedrich³ first noticed that germanium tetrachloride was immiscible with and unaffected by concentrated sulfuric acid. Dennis and Hance⁴ observed that concentrated nitric acid attacked germanium tetrachloride, although somewhat slowly. The effect of concentrated hydrochloric acid on germanium tetrachloride has not been studied, while it is known that arsenious chloride has a high solubility in this acid.⁵

Preliminary experiments showed that concentrated sulfuric acid was not suitable for the extraction of arsenious chloride from germanic chloride because of the low solubility of arsenious chloride in the acid. Germanium tetrachloride was found to be practically insoluble in concentrated hydrochloric acid. The distribution of arsenious chloride between concentrated hydrochloric acid and germanium tetrachloride was investigated and the extraction of arsenious chloride from germanic chloride by means of concentrated hydrochloric acid studied as a purification method.

¹ Dennis and Johnson, *J. Am. Chem. Soc.*, **45**, 1380 (1923).

² Abrahams and Müller, *ibid.*, **54**, 86 (1932).

³ Friedrich, *Monatsh.*, **14**, 519 (1893).

⁴ Dennis and Hance, *J. Am. Chem. Soc.*, **44**, 307 (1922).

⁵ Treadwell and Mussler, *Helv. Chim. Acta*, **5**, 812 (1922).

Experimental Part

The apparent solubility of germanium tetrachloride and of arsenious chloride in hydrochloric acid of various concentrations was determined in order to learn the concentration of acid most suitable for extraction purposes. The term "apparent solubility" is used advisedly since it cannot be said that no hydrolytic decomposition of the chlorides takes place on dissolving.

Materials.—Germanium tetrachloride was prepared from the mineral germanite. The mineral was decomposed by concentrated nitric acid. This served to remove the great bulk of copper, iron and sulfur, leaving a siliceous residue small in bulk and rich in germanium dioxide. The residue was treated with concentrated hydrochloric acid and germanium tetrachloride distilled and collected under iced water. Hydrolysis of the chloride gave the dioxide, which was contaminated with arsenic. This was removed by the sulfide method. The pure germanium sulfide obtained was hydrolytically converted to the dioxide⁶ and the latter reconverted to the tetrachloride. No attempt was made to remove hydrogen chloride from the product since it was to be used in experiments in which it would be shaken with hydrochloric acid. The other materials were Baker's C. P. Analyzed Chemicals. Arsenic-free sulfuric and hydrochloric acids were used at all times when the avoidance of traces of this element was desired.

Methods of Analysis.—Determinations of germanium and separations of germanium from arsenic were made according to the method of Abrahams and Müller.²

Arsenic was determined as magnesium pyroarsenate according to the method of McNabb.⁷

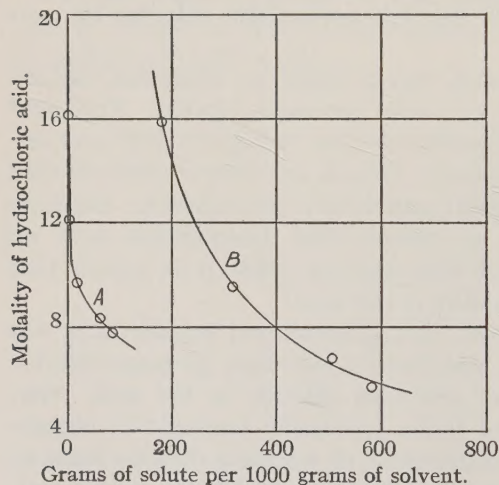


Fig. 1.—Curve A, germanium tetrachloride;
Curve B, arsenious chloride.

analysis. A similar series of determinations was made in which arsenious chloride was the solute. The results of the analyses are given in Tables I and II, and represented graphically in Fig. 1.

The solubility of both chlorides increases as more dilute acid is used as

⁶ Müller and Eisner, *Ind. Eng. Chem., Anal. Ed.*, **4**, 134 (1932).

⁷ McNabb, *J. Am. Chem. Soc.*, **49**, 1451 (1927).

solvent. Germanic chloride is almost insoluble in the most concentrated acid used, while arsenious chloride has a very high solubility in the same solvent. The diluted acid, which dissolves almost one hundred times as much germanium tetrachloride as the concentrated acid, dissolves only about twice as much arsenious chloride as the concentrated acid. This is clearly shown in Fig. 1. Concentrated hydrochloric acid is thus most suitable for the extraction of arsenious chloride from germanium tetrachloride.

TABLE I

APPARENT SOLUBILITY OF GERMANIC CHLORIDE IN HYDROCHLORIC ACID AT 25°

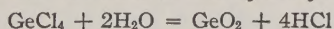
	Molality of HCl	G. GeCl_4 /1000 g. solvent	Molality of GeCl_4
1	16.14	0.882	0.00411
2	12.08	1.826	.00852
3	9.72	17.84	.0832
4	8.32	61.83	.288
5	7.77	85.36	.398

TABLE II

APPARENT SOLUBILITY OF ARSENIOS CHLORIDE IN HYDROCHLORIC ACID AT 25°

	Molality of HCl	G. AsCl_3 /1000 g. solvent	Molality of AsCl_3
1	15.87	181.5	1.00
2	9.52	316.7	1.75
3	6.80	506.0	2.79
4	5.71	582.5	3.21

Since germanium tetrachloride proved to be so slightly soluble in concentrated hydrochloric acid it seemed possible that it would be precipitated from an aqueous germanium dioxide solution on saturation with hydrogen chloride. The production of liquid germanic chloride without distillation in the reversal of the hydrolysis reaction



has not been reported. The experiment is also of interest as a further test of the solubility of germanic chloride in concentrated hydrochloric acid. A solution of germanium dioxide was chilled in crushed ice and saturated with hydrogen chloride. Germanium tetrachloride was produced, separated from the hydrochloric acid by means of a separatory funnel, and identified by its boiling point. The hydrochloric acid was analyzed for its germanium content. It contained only 0.348 g. of germanium tetrachloride per 1000 g. of solvent, which compares favorably with values obtained later for the solubility of germanium tetrachloride in concentrated hydrochloric acid at 0° (see Table IV).

The Distribution of Arsenious Chloride between Germanium Tetrachloride and Concentrated Hydrochloric Acid

Apparatus.—On account of the high vapor pressures of the liquids involved it was necessary to work at a low temperature. A jacketed

separatory funnel was obtained for use as the vessel in which equilibrium conditions were attained. The outer jacket could be packed with crushed ice, keeping the inner compartment at 0° . The inner compartment was cylindrical in shape and set off center, causing one side to nearly touch the wall of the outer jacket. In this way the ice did not prevent vision into the inner compartment.

Experimental Procedure.—Approximately 10 cc. of arsenious chloride, 50 cc. of germanium tetrachloride and 75 cc. of concentrated hydrochloric acid were placed in the apparatus. The acid used contained 36.63% hydrogen chloride. The apparatus was shaken for two minutes and then allowed to stand for three minutes. This was repeated for an hour and a half, then the apparatus was allowed to stand for half an hour to give complete settling of the germanium tetrachloride layer. Samples of the upper hydrochloric acid layer were sealed in thin-walled glass bulbs for accurate weighing. It was not necessary to weigh samples of the germanium tetrachloride layer. Portions were run under cold water and allowed to hydrolyze. Pellets of pure sodium hydroxide were added slowly until the solution reacted alkaline to phenolphthalein. Warming caused rapid solution of the germanium dioxide which had resulted from the hydrolysis of the chloride. The solutions thus obtained were analyzed for both arsenic and germanium.

After the first set of samples had been taken the hydrochloric acid layer was siphoned out of the apparatus and replaced by fresh acid. Repetition of the shaking and sampling procedure gave a second set of samples in which the amounts of arsenious chloride present in the two layers were necessarily smaller. In the same way a third set of samples was obtained. This made possible the determination and comparison of values for the distribution coefficient obtained with varying amounts of arsenious chloride distributed.

Results of the analyses and the values of the distribution coefficient are given in Table III. Variation of the distribution coefficient is expressed graphically in Fig. 2. Experiments 4A and 4B were carried out under a different procedure. Germanium tetrachloride, arsenious chloride and concentrated hydrochloric acid were placed together and sealed in large bulbs. These were fastened to a mechanical shaker placed in a

TABLE III
DISTRIBUTION COEFFICIENT AT 0°

	Molality of AsCl_3 in HCl layer, M_1	Molality of AsCl_3 in GeCl_4 layer, M_2	$K = M_1/M_2$
1	0.3298	0.3571	0.9235
2	.1707	.1617	1.056
3	.08012	.06489	1.235
4A	.2323	.2468	0.9413
4B	.2356	.2475	.9519

cold room regulated at 0° , with a maximum variation of 5° . After five days the bulbs were taken off the shaker and kept in crushed ice, still in the cold room, for an additional twenty-four hours. This gave a final equilibrium temperature of 0° . Samples of the two layers were taken as in the previous experiments.

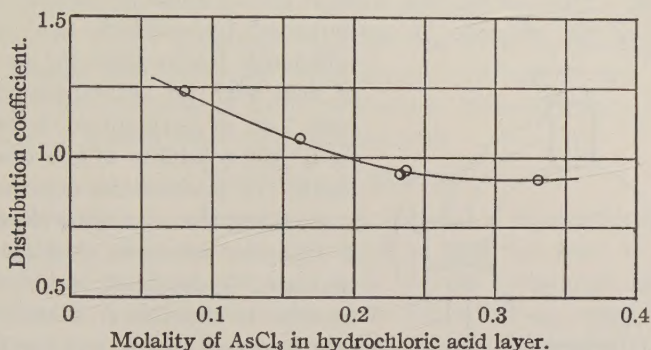


Fig. 2.—Variation of the distribution coefficient with the amount of arsenious chloride distributed between concentrated hydrochloric acid and germanium tetrachloride at 0° .

The values of the distribution coefficient vary inversely with the amounts of arsenious chloride distributed between the two layers. The rate of extraction, removal of arsenious chloride from germanic chloride, increases as the extraction proceeds, although the coefficient is small in all cases. The fact that the values obtained in experiments 4A and 4B, in which six days were allowed for the attainment of equilibrium, fall in the proper relation to the other values, is an indication that equilibrium conditions had been reached in all experiments. This is clearly shown in Fig. 2.

The concentration of germanium tetrachloride in the concentrated hydrochloric acid layers was determined. The results are given in Table IV. The solubility of germanic chloride in concentrated hydrochloric acid at 0° is shown to be considerably less than at 25° (compare No. 1, Table I).

TABLE IV

CONCENTRATION OF GERMANIC CHLORIDE IN THE CONCENTRATED HYDROCHLORIC ACID LAYERS AT 0°

G. concd. HCl + GeCl_4	GeCl_4 found, g.	GeCl_4 , %	Average of best 3	Molality of GeCl_4
10.2960	0.00291	0.0283		
8.1893	.00322	.0393		
13.8241	.00502	.0363		
12.5074	.00455	.0364	0.0373	0.00174

Purification Experiment

The coefficient for the distribution of arsenious chloride between concentrated hydrochloric acid and germanium tetrachloride is so small that a sample of germanic chloride containing arsenious chloride must be shaken with several portions of acid in order to remove the arsenic completely. This can be done without loss of much germanium since the solubility of the chloride in concentrated hydrochloric acid at 25° is

sufficiently low to allow the use of a liter of acid with an accompanying loss of only 1 g. of germanium tetrachloride. At 0° the solubility is less than half as much. A purification experiment was made using the apparatus shown in Fig. 3. Impure germanic chloride and concentrated hydrochloric acid are shaken together in chamber A, allowed to separate into two layers, and the lower germanic chloride layer then run into chamber B. The acid layer is poured out of the apparatus and the germanic chloride run back into A from B, after proper adjustment of the three-way stopcock at C. Fresh acid is now added. The process involves inversion of the appa-

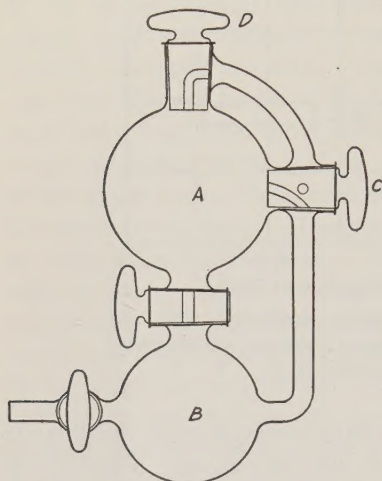


Fig. 3.—Extraction apparatus.

ratus and removal of the stopper at D while the acid is being poured out.

Approximately 35 cc. of germanic chloride containing 1.16% of arsenious chloride was treated with 70 cc. of chilled acid. The same amount of acid was used for the second extraction and 100 cc. in each of the successive treatments, each extraction requiring about five minutes. After the eighth extraction the acid no longer gave a test for arsenic and no arsenic could be detected in the germanium tetrachloride. On the basis of the small amount of arsenic required to discolor germanium sulfide,³ and since the last portion of acid used gave a pure germanium sulfide precipitate when treated with hydrogen sulfide, it was calculated that the germanium tetrachloride layer could not have contained more than one part of arsenious chloride for each two million parts of germanium tetrachloride.

Experiments with the Chlorides of Antimony, Tin and Titanium.—A study of the behavior of chlorides of elements closely related to germanium and arsenic, with concentrated hydrochloric acid in the presence of germanium tetrachloride, is interesting. Antimony pentachloride, stannic chloride and titanium tetrachloride were chosen. These are known to be soluble in concentrated hydrochloric acid.

Approximately 25 cc. of germanic chloride was placed in the jacketed

separatory funnel and 1 cc. of antimony pentachloride added. This caused a slight turbidity which disappeared on treatment with 100 cc. of chilled acid. The apparatus was kept cold, shaken for fifteen minutes, and allowed to stand for thirty minutes. Portions of the germanic chloride layer were drawn off under cold water and the resulting solutions tested with hydrogen sulfide. No antimony could be detected. Similar experiments in which germanic chloride had been contaminated with stannic chloride and titanium tetrachloride resulted in the complete removal of these substances from germanium tetrachloride by a single extraction with concentrated hydrochloric acid.

Discussion of Results

The insolubility of germanium tetrachloride in concentrated hydrochloric acid is a characteristic difference in behavior from that of the tetrachlorides of titanium, tin and lead. These compounds are soluble in concentrated hydrochloric acid with formation of complex chloro acids of the type H_2MeCl_6 . The corresponding germanium chloro acid has not been prepared. This behavior of germanic chloride is not only an interesting distinction from the anhydrous chlorides of its type, but also likens germanic chloride to the similarly inactive tetrachloride of carbon. The complete removal of the chlorides of antimony, tin and titanium from germanic chloride in one treatment with concentrated hydrochloric acid is an interesting distinction from the behavior of arsenic. This can only be well explained by the assumption of a definite formation of the chloro acids of these elements, which must be insoluble in the germanium tetrachloride layer.

Sufficient data for the calculation of the constant for the distribution of arsenious chloride between concentrated hydrochloric acid and germanic chloride are not available. The constant could only be calculated provided the concentration of simple arsenious chloride molecules in each layer were known. The values for the coefficient reported here were calculated from the total concentration of arsenic found in each layer. At present there is no information available regarding the ionization or possible association of arsenious chloride dissolved in germanium tetrachloride or concentrated hydrochloric acid. The actual conditions existing in these systems may be the subject of further investigation.

If proper apparatus for the preparation of large quantities of pure germanium tetrachloride by the distillation method is not available, the method of extracting arsenious chloride by means of cold concentrated hydrochloric acid may be conveniently used.

Summary

1. Arsenious chloride can be removed completely from germanium tetrachloride by extraction with concentrated hydrochloric acid.

2. The apparent solubility of germanium tetrachloride, and of arsenious chloride, in hydrochloric acid of various concentrations, has been determined. Germanium tetrachloride is practically insoluble in concentrated hydrochloric acid.

3. The distribution of arsenious chloride between concentrated hydrochloric acid and germanium tetrachloride has been studied.

4. The chlorides of antimony, tin and titanium may be removed from germanium tetrachloride by a single extraction with concentrated hydrochloric acid.

